# Studies on Behavior of Tritium in Components and Structure Materials of Tritium Confinement and Detritiation Systems of ITER

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**Abstract.** The confinement and removal of tritium are the key subjects for safety of ITER. The ITER buildings are confinement barriers of tritium. In a hot cell, tritium is often released, as vapor and is in contact with the inner walls. Also those of an ITER tritium plant building will be exposed to tritium in an accident. The tritium released in the buildings is removed by the Atmosphere Detritiation Systems (ADS), where the tritium is oxidized by catalysts and is removed as water. Special gas of $SF_6$ is used in ITER, and is expected to be released in an accident such as fire. Although the $SF_6$ gas has the potential as a catalyst poison, the performance of ADS with the existence of $SF_6$ has not been confirmed yet. Tritiated water is produced in the regeneration process of ADS, and is subsequently processed by the ITER Water Detritiation System (WDS). One of the key components of WDS is an electrolysis cell. To overcome the issues in a global tritium confinement, a series of experimental studies have been carried out as an ITER R&D task: 1) tritium behavior in concrete; 2) effect of $SF_6$ on performance of ADS; and 3) tritium durability of electrolysis cell of ITER-WDS. 1) The tritiated water vapor penetrated only up to 50 mm into the concrete from the surface in six months' exposure. The penetration rate of tritium in the concrete was thus appreciably slow, the isotope exchange capacity of cement paste plays an important role at tritium trapping and penetration in concrete materials when concrete is exposed to tritiated water vapor. It is required to evaluate the effect of the lining on the penetration rate quantitatively from the actual tritium tests. 2) The $SF_6$ gas decreased the detritiation factor of ADS. Since the effect of the $SF_6$ depends on its concentration closely, the amount of $SF_6$ released into the tritium handling area in an accident should be deduced by some ideas of the arrangement of components in the buildings. 3) It was expected that the electrolysis cell of ITER-WDS could endure 3 years' operation under the ITER design conditions. Measuring the concentration of the fluorine ions could be a promising technique for monitoring the damage of the electrolysis cell.

## 1. Introduction

The confinement and removal of tritium are the key subjects for safety of ITER, and tritium should be well controlled so that it is not released excessively into the atmosphere to prevent workers and public from excess exposure. Tritium will be handled under a multiple confinement system in a fusion reactor and each level of confinement will have its own detritiation system [1]. This concept of the multiple confinement system has been adopted in many tritium facilities in the world successfully [2,3]. Tritium Process Laboratory (TPL) of the Japan Atomic Energy Agency (JAEA) is a licensed to handle 22.2 PBq of tritium, which has also a multiple confinement system [4], and it has been accumulating the safety experiences for almost 20 years without any accidental tritium release to rooms and the environment since its foundation. A room and/or a building will be important as a final confinement barrier of tritium to the environment. Also, it will be important to grasp the tritium contamination in the concrete because the concrete was selected as the construction material of ITER tritium facilities and the hot cell and it was exposed by tritium during normal maintenance operations and any accidents. However, the data are scarce, especially on the penetration of tritium into the concrete of the wall materials. The tritium released in the buildings is removed by the Atmosphere Detritiation Systems (ADS), where the tritium is oxidized by catalysts and is removed as water. Special gas of $SF_6$ is used in ITER as insulation gas for NBI, and is expected to be released in an accident such as fire. In the previous studies, a series of performance tests of the typical Pt catalyst have been performed under co-existing of CO or $CO_2$ gases as main generated gas at fire. No degradation of oxidation performance of hydrogen and methane was observed under co-existing of CO or $CO_2$ even up to 10-20% in air [5]. Although the $SF_6$ gas has the potential as a catalyst poison, the performance of ADS with the existence of $SF_6$ has not been confirmed yet. Tritiated water is produced in the regeneration process of ADS, and is subsequently processed by the ITER Water Detritiation System (WDS). One of the key components of WDS is an Solid-polymer-electrolyte (SPE) water electrolysis [6-8]. The SPE is attractive in electrolytic process of radioactive liquid waste because it can electrolyze liquid waste directly without alkaline addition. The SPE water electrolyzer [9] is planned to be used in the WDS [10] of the ITER [11]. Durability of polymers in electrolyzer by radiation is a debatable point. In ITER, an electrolyzer is planed to be replaced every two years, that is, the electrolyzer should keep its performance during two years operation in tritiated water of 9TBq/kg, the design tritium concentration of ITER. The tritium exposure of 9TBq/kg for two years is corresponding to irradiation of 530 kGy. Therefore, the effect of tritium exposure on organic polymers used in the electrolyzer should carefully be discussed. However, there is no data on the durability of the cell exposed to tritium. To overcome the issues in a global tritium confinement, a series of experimental studies have been carried out as an ITER R&D task: 1) tritium behavior in concrete; 2) effect of $SF_6$ on performance of ADS; and 3) tritium durability of electrolysis cell of ITER-WDS.

## 2. Experimental

### 2.1 Tritium behavior in concrete

Table I shows the experimental conditions of the exposure experiment for the concrete. The chamber is $2.7^{W}$m X $1.2^{D}$m X $2.4^{H}$m leak-tight box. The atmosphere in the chamber is controlled by the tritium concentration of 740~1100Bq/$cm^3$, and the moisture concentration of less than 10000 ppm. The used samples were the standard concretes, cement pastes and mortars. In order to prevent the penetration of the tritiated water vapor from the side and the bottom of sample (small size of cement paste), the sample was covered the side and the bottom with silicon paste, natural rubber latex and Teflon tape. It was also covered with epoxy paint for the standard samples (Large size of the concrete, cement paste and mortar). The samples were exposed in the chamber at the maximum for 6 months. After exposures, each sample was drilled and sliced, and then the sliced samples in each section were soaked in water as shown in Fig.1. The captured tritium in the sample was measured by a liquid scintillation counter.

Table I Experimental conditions of tritium exposure for concrete samples

| | |
|---|---|
| Tritium concentration in the chamber | 740 ~ 1100 Bq/$cm^3$ (HTO) |
| Moisture concentration | Less than 10000ppm |
| Exposure time | 6 months |
| Materials | Concrete<br>Cement paste<br>Mortar |
| Size of sample materials | Small $13mm^{\phi}$x$100mm^{L}$<br>Large $100mm^{\phi}$x$100mm^{L}$ |

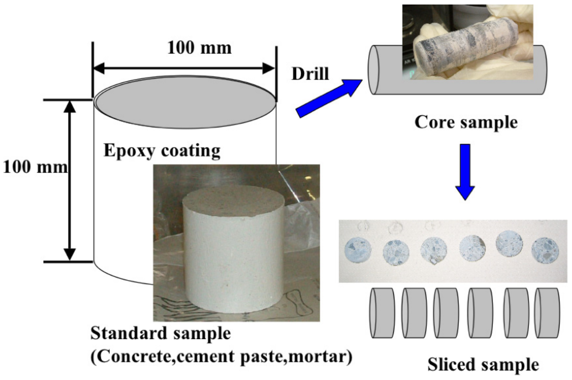

*Fig.1 Standard samples (concrete, cement paste, mortar)*

### 2.2 Effect of $SF_6$ on performance of ADS

The conceptual layout and the specifications of the oxidation performance apparatus as well as the experimental conditions are shown in Fig. 2 and Table II, respectively. The performance tests of ADS was carried out with air containing ~1% of hydrogen, ~1% of methane and ~1% of $SF_6$. The detritiation system consists of two mass flow controllers (MFC) and two oxidation catalyst beds (473 K and 773 K (0.5%Pt – $Al_2O_3$)) for converting hydrogen isotopes and tritiated methane to water vapor as the usual detritiation system. The performance of oxidation catalyst beds of the detritiation system for hydrogen and methane under co-existence of $SF_6$, which are introduced at the accident, was investigated. Detritiation factor (D.F.) was evaluated with the ratios of $H_2$ or $CH_4$ concentration of inlet and outlet of two catalyst beds (473 K and 773 K). Concentrations of gases such as $H_2$, $CH_4$ and $SF_6$ were measured by gas chromatography and mass spectrometry. The deposits collected in the outlet of 773 K catalyst bed were also measured by SEM-EDX.

### 2.3 Tritium durability of electrolysis cell of ITER-WDS

Seven organic polymers were irradiated by the gamma ray: five kinds of ion exchange membrane (Nafion® N112, N115, N117, NE1110, NE1135 by DuPont); and two kinds of PTFE (PFA 500LP: Perfluoroalkoxyethylene co-polymer, FEP 750A: Tetrafluoroethylene-Hexafluoroethylene co-polymer by DuPont).
A structure of test stand for the irradiation of the gamma rays is illustrated in Fig. 3. A specimen was cut from each polymer with size and shape determined by the Japanese Standards for tensile tests (ASTMD-1822L). The specimen was then set in a laminate film bag. The laminate film is the thin aluminum foil coated with polyethylene and polyester, and it can block permeation of oxygen and water vapor. The specimen thus prepared was then irradiated by the gamma rays at 10 kGy/h at room temperature. After the specimen was taken out from the test stand, a series of tensile tests was carried out. The pH value, electrolytic conductivity, electrolytic resistivity, quantity of dissolved fluorine in the soaked solution were measured by pH meter, EC meter and ion meter, respectively. The ion exchange capacity was measured as follows. A piece of sample was cut from the specimen irradiated, and was immersed into hydrochloric acid. By replacing the hydrochloric acid several times, a sulfonic acid group in the sample was changed from $SO_3H$ to $SO_3^-H^+$ by hydrolyze. The sample was then washed with distilled water to remove hydrochloric acid. After the washing, the sample was immersed into a solution of NaCl. The ion $H^+$ was replaced to $Na^+$, and the $H^+$ exuded from the sample to the solution. An amount of $H^+$ was measured by titration with NaOH. The ion exchange capacity was thus evaluated through the above procedures.

Table II Experimental Conditions of effect of $SF_6$ gas on performance of tritium removal facilities.

| Ambient Gas | Dry Air |
|---|---|
| Concentration of $H_2$ | 0~1% |
| Concentration of $CH_4$ | 0~1% |
| Concentration of $SF_6$ | 0~1% |
| Catalyst | 0.5%Pt-alumina |
| Temperature and Spatial Velocity (SV) | 200ºC (SV:6000 [$h^{-1}$])<br>500ºC (SV:3000 [$h^{-1}$]) |
| Flow Rate | ~0.06 $m^3/h$ (1L/min) |

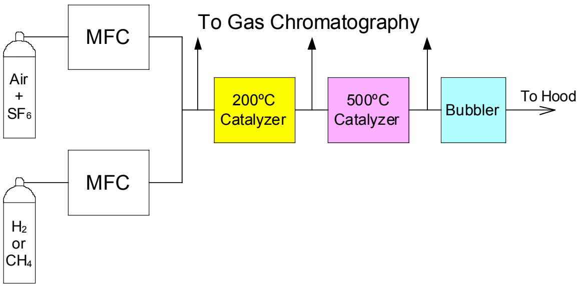

*Fig.2 Schematic diagram of experimental apparatus.*

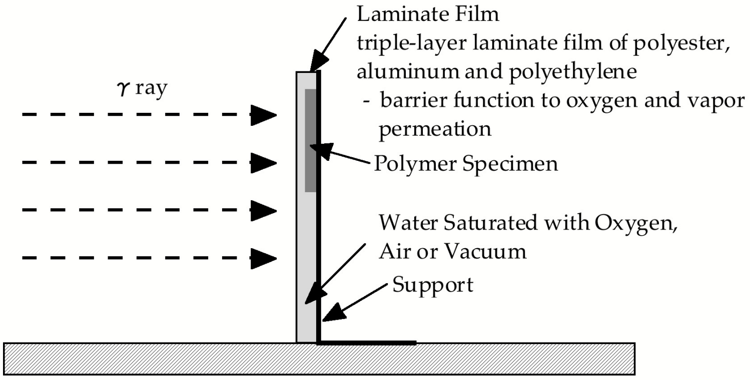

*Fig. 3 Structure of test stand for the irradiation of gamma ray.*

## 3. Results and Discussions

### 3.1 Tritium behavior in concrete

The experimental results obtained from small size samples were shown in Table III after consideration of H/T ratio. The isotope exchange capacity in this study means total amount of water used as isotope exchange reaction in concrete materials. Tritium isotope exchange capacity to the cement paste was much larger than the isotope exchange capacity of metal materials to be used in the construction of fusion facilities.

The isotope exchange capacity observed for the cement paste sample in this study is about two times larger than that of mortar and about ten times larger than that of sand. This result means that the isotope exchange capacity of mortar is mainly decided by the cement paste and the isotope exchange capacity to the mortar is estimated by the following equation.

$$S_{mortar} = S_{cement} \times x_{cement} + S_{sand} \times x_{sand} \,, \qquad (1)$$

where $S$ is the isotope exchange capacity, $x$ is a ratio of material indicated by subscript in mortar, respectively.

Fig. 4 shows comparison of tritium distribution observed in the core part of large size sample of cement paste, mortar and concrete. The histogram in Fig. 4 expresses the average amount of tritium trapped to a disc piece cut off from the column specimen. It is known from this figure that tritium penetration from the side wall gives no effect on the tritium profile in the core part of the large size specimen though some penetration is observed from the bottom surface. Mortar and concrete have the same transfer rate of tritium as cement paste, even though the isotope exchange capacity of mortar or concrete is less than half of cement paste.

Table III Isotope exchange capacity in concrete materials

| | Isotope exchange capacity [Bq/g] |
|---|---|
| Cement paste | $3.97 \times 10^{13}$ |
| Mortar | $1.50 \times 10^{13}$ |
| Sand | $6.12 \times 10^{11}$ |

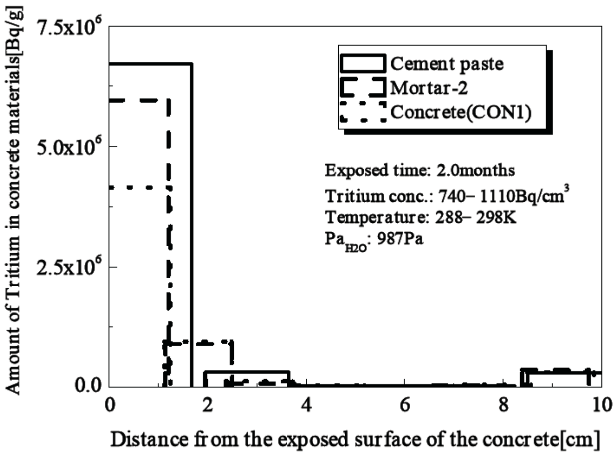

*Fig. 4 Change of tritium concentration profile in core part of concrete materials.*

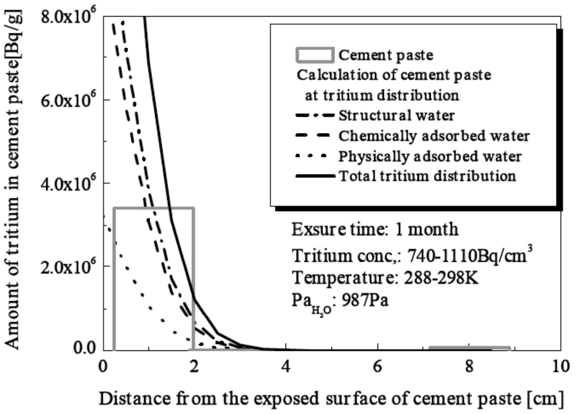

*Fig.5 Comparison of experimental results and calculation about tritium concentration profile in cement paste.*

Because sand or aggregate has smaller exchange capacity, it is considered for this reason that the specific surface area of mortar and concrete effective for adsorption and isotope exchange reaction decreases relatively by addition of sand or aggregate. Change of chemical composition with time may affect the tritium behavior because Terashima et al. reported that the diffusion coefficient of tritiated water in concrete is smaller than that of mortar and cement paste. It is obtained that the penetration length of tritium in six months is only 50mm from the exposure surface. This observation indicates that the tritium penetration along the core axis is so slow because cement materials have rather large isotope exchange capacity.

Fig. 5 shows comparison between experimental results of cement paste with large size samples and calculation of cement paste using the same mass transfer properties as the calculation of small size. The physically adsorbed water, chemically adsorbed water and structural water in Fig. 5 are defined by Takata et al.. It is found from Fig. 5 that the estimated value for total tritium trapped in the large size cement paste does not agree with experimental results, while the estimated value for of tritium trapped to structural water gives good agreement with experimental value. It is considered that temperature rise at drilling operation may release tritium trapped as chemically adsorbed water.

### 3.2 Effect of $SF_6$ on performance of ADS

The temperature dependency of the decomposition reaction of $SF_6$ is shown in Fig. 6. As shown in this figure, the decomposition reaction of $SF_6$ occurred from 623 K of the temperature of the catalyst bed. Therefore, the oxidization performance of hydrogen will not be affected at 473 K, the operation temperature of the first catalyst bed.

The concentrations of gases ($H_2$, $SF_6$ and decomposed gas of $SF_6$) at the outlet of 773 K of catalyst bed is plotted against the total amount of $SF_6$ in Fig. 7 for the oxidation performance

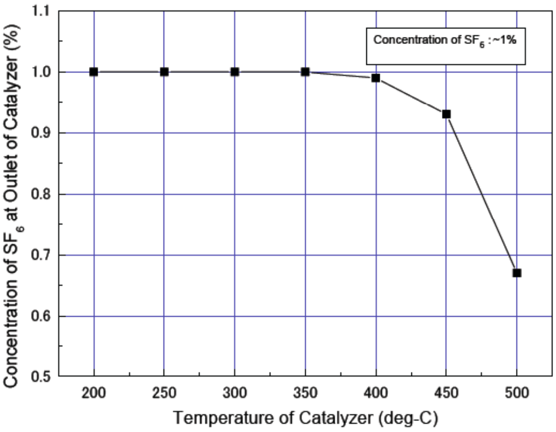

*Fig. 6 Decomposition behavior of 1% $SF_6$ in the air by the catalyst bed.*

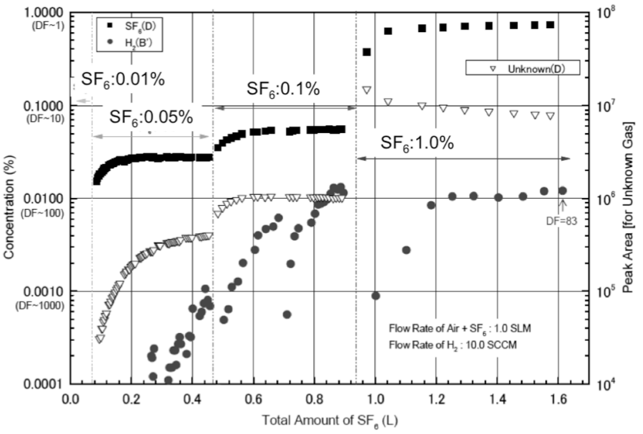

*Fig. 7 The change of the concentration of each gas ($H_2$, $SF_6$ and decomposed gas of $SF_6$) at the outlet of 773K of catalyst bed for the oxidation performance test of 1% hydrogen.*

test of 1% hydrogen. When 0.01% of $SF_6$ was introduced with 1% of hydrogen, $SF_6$ was decomposed at 773 K, the operation temperature of the catalyst bed. However, since the decomposed gas of $SF_6$ and $SF_6$ were so small, 1% hydrogen could not be detected by GC. When 0.05% or more of $SF_6$ was introduced with 1% of hydrogen, $SF_6$ was similarly decomposed at 773 K, and hydrogen was also simultaneously detected at the outlet of the 773 K catalyst bed. It was considered that hydrogen was oxidized to water vapor at the 473 K catalyst bed and then the oxidized water vapor was reduced by the decomposed gas of $SF_6$ at the 773 K catalyst bed. Consequently, detritiation factor (D.F.) decreased down to ~50 from more than 1000.

After termination of $SF_6$, D.F. was recovered up to >100 immediately. Finally, D.F. was recovered up to >10000 in about 3 days at the flow rate of 1 L/min for air and 10 $cm^3$/min for hydrogen. It suggests that if $SF_6$ is not continuously released, D.F. can be recovered immediately for the ITER detritiation systems.

After the experiment for the oxidation performance of hydrogen under co-existence of $SF_6$, unknown deposits collected at the outlet of the 773 K catalyst bed were analyzed by SEM-EDX. As the results, the peak of elements of stainless steel (SS) which were component materials for experimental apparatus, and S were detected for all points. The peak of Pt, which was component for catalyst, was detected only at one point. The peak of F cannot be distinguished from that of Fe by this method. It was considered that $SF_6$ was decomposed to sulfurous acid gas etc and then the sulfurous acid gas was corroded the pipe of SS.

In order to identify the decomposed gas of $SF_6$, the mass analysis was carried out at the inlet and outlet of the 473 K catalyst bed and the outlet of the 773 K catalyst bed. The introduced gas was air mixed with 1% of $SF_6$ and 1% hydrogen. In the result of the mass analysis at the inlet of the 473 K catalyst bed, $SF_x$ (x = 1 to 5) was detected. At the outlet of the 473 K catalyst bed, $SF_x$ (x = 1 to 5) was also detected, suggesting that $SF_6$ was not decomposed by this catalyst. At the outlet of the 773 K catalyst bed, species like $SO_2F_2$ were detected, indicating that some $SF_6$ was decomposed by the 773 K catalyst bed. It was considered that $SF_6$ was decomposed to $SF_4$ and $SO_2F_2$. The reactions occurred at the 773 K catalyst bed may be given out as follows,

$$2SF_6 + 2H_2O \rightarrow 2SF_4 + 4HF + O_2$$
$$SF_4 + 2H_2O \rightarrow SO_2F_2 + 2HF + H_2$$
$$(SF_4 + H_2O \rightarrow SOF_2 + 2HF$$
$$SOF_2 + H_2O \rightarrow SO_2 + 2HF)$$

The above reactions suggest that the generated water vapor was reduced by $SF_6$ and $SF_4$, which is decomposed by $SF_6$ at the 773 K catalyst bed. As the result, D.F. was decreased down to ~50 from more than 1000.

The $SF_6$ gas will not affect the oxidation performance when its concentration is less than 0.01%. It is required to monitor continuously and to reduce the amount of the $SF_6$ gas released into the tritium handling area for the minimization of the poison effect by some ideas of the arrangement of components in the buildings. It is also required to evaluate the amount of $SF_6$ gas released in detail by a set of accidental analysis.

### 3.3 Tritium durability of electrolysis cell of ITER-WDS

#### 3.3.1 Distinctive radiation durability of Nafion®

Elongation at break vs dose for Teflon and Nafion N117 was measured. FEP750A is a typical Teflon resin balancing high mechanical strength and processing, whereas PFA500LP is an improved Teflon resin that is directed to higher upper limit of operating temperature than that of FEP [12]. Nafion is composed of a main chain of PFA and branches with sulfonic acid [12]. Elongation at break is an index of polymer degradation. It becomes lower as polymer is degrading. Judging from the measurement results, Nafion has considerably higher irradiation durability than that of FEP and PFA. Since the strength of polymer is interpreted to depend on its main chain generally and the main chain of Nafion is PFA, degradation of mechanical strength of Nafion by gamma-ray irradiation was significantly distinguished from that of FEP and PFA.

### 3.3.2 Effect of Nafion® grade on degrading behaviors

Tensile strength vs dose for various Nafion irradiated by gamma ray is shown in Fig. 8. The specimen of N112, N115, N117, NE1110, NE1135 after irradiation had average thickness of 51, 139, 180, 292, 83 $\mu$ m, respectively. No considerable difference in the degrading behavior was observed among various grades. The strength gradually decreases with increase of dose under soaking condition. From the viewpoint of degrading ratio defined as $S/S_0$, where S and $S_0$ are tensile strength at 500 or 850 kGy and the corresponding value at 0kGy, we observed a tendency that degrading was promoted as the specimen were thinner. The observation corresponds to the our proposal degrading mechanism that only a few layers from Nafion surface degrade due to dissolved oxygen. In the electrolysis cell, the membrane suffers almost no load. Therefore, durability of the membrane concerning the tensile strength against the irradiation was well demonstrated up to 850 kGy.

Ion exchange capacity vs dose for various Nafion irradiated by gamma ray is shown in Fig. 9. Although we observed slight tendency that decrease in ion exchange capacity was promoted as the specimen were thinner, it can be pointed out that degrading of ion exchange capacity of various grades were less influential. Therefore, durability of the membrane concerning ion exchange capacity against the irradiation was also well demonstrated up to 850 kGy.

Quantity of dissolved fluorine vs dose for various Nafion irradiated by gamma ray is measured. Although the behaviors of the quantity of dissolved fluorine were varied by Nafion grade to a certain extent, we observed that the quantity of dissolved fluorine from each grade of Nafion correlates closely with dose by a quadratic function. It was also found that both the tensile strength and ion exchange capacity correlate with the quantity of dissolved fluorine, respectively. This fact can apply in the remote, online and nondestructive inspection of ion exchange membrane by the monitoring the quantity of dissolved fluorine. Electrolytic conductivity and resistivity vs dose for Nafion N112 irradiated by gamma ray is also measured. Degrading of ion exchange membrane leads the substantial change in pH and

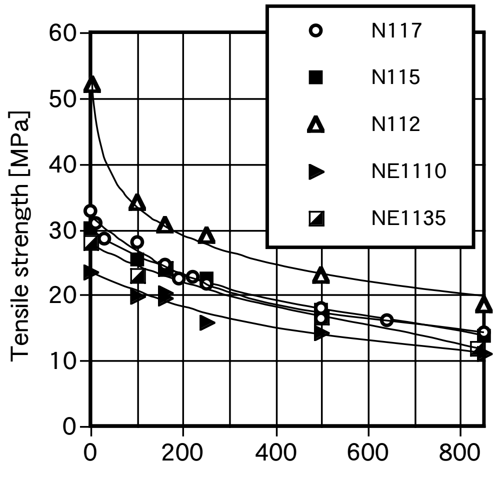

*Fig. 8 Tensile strength vs dose for various Nafion irradiated by gamma ray.*

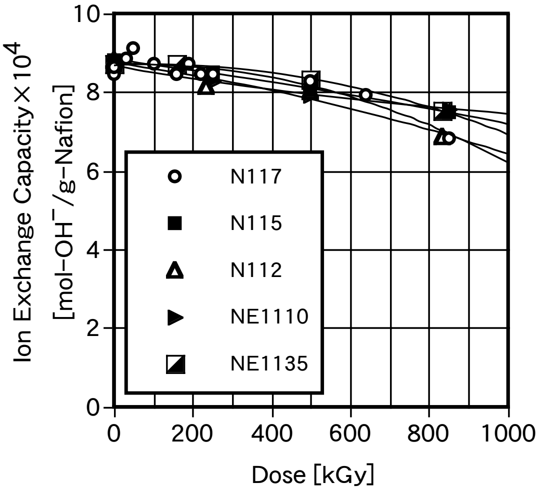

*Fig. 9 Ion exchange capacity vs dose for various Nafion irradiated by gamma ray*

electrolytic conductivity and resistivity. They have a correlation with tensile strength and ion exchange capacity. Therefore, their monitoring can apply in the remote, online and nondestructive inspection of ion exchange membrane in combination with the monitoring the quantity of dissolved fluorine.

## 4. Conclusion

1) The tritiated water vapor penetrated only up to 50 mm into the concrete from the surface in six months' exposure. The penetration rate of tritium in the concrete was thus appreciably slow, the isotope exchange capacity of cement paste plays an important role at tritium trapping and penetration in concrete materials when concrete is exposed to tritiated water vapor. It is required to evaluate the effect of the lining on the penetration rate quantitatively from the actual tritium tests.

2) The $SF_6$ gas decreased the detritiation factor of ADS. Since the effect of the $SF_6$ depends on its concentration closely, the amount of $SF_6$ released into the tritium handling area in an accident should be deduced by some ideas of the arrangement of components using $SF_6$ in the buildings.

3) It was expected that the electrolysis cell of ITER-WDS could endure 3 years' operation under the ITER design conditions. Measuring the concentration of the fluorine ions could be a promising technique for monitoring the damage of the electrolysis cell.

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